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(54) Title: TEMPERATURE ADAPTABLE TEXTILE FIBERS AND METHOD OF PREPARING SAME		
(57) Abstract <p>Temperature adaptable textile fibers in which phase-change or plastic crystalline materials are filled within hollow fibers or impregnated upon non-hollow fibers. The fibers are produced by applying solutions or melts of the phase-change or plastic crystalline materials to the fibers. Cross-linked polyethylene glycol is especially effective as the phase change material, and, in addition to providing temperature adaptability, it imparts improved properties as to soil release, durable press, resistance to static charge, abrasion resistance, pilling resistance and water absorbency.</p>		

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1 TEMPERATURE ADAPTABLE TEXTILE FIBERS AND METHOD OF
2 PREPARING SAME

3 BACKGROUND OF THE INVENTION

4 Field of the Invention

5 This invention relates to modified textile fibers.

6 Description of the Prior Art

7 The concept of preparing a temperature-adaptable
8 hollow fiber has been previously demonstrated and
9 described in U.S. Patent 3,607,591. This invention
10 incorporates a gas into liquid inside the fiber that
11 increases the diameter of the fiber and thus increases
12 its thermal insulation value when the liquid solidifies
13 and the solubility of the gas decreases. However, this
14 invention exhibits serious limitations. It is limited to
15 use with only hollow textile fibers and is only
16 applicable in cold weather situations, i.e., when the
17 environmental temperature drops below the freezing point
18 of the liquid in the fiber. Furthermore, this modified
19 hollow fiber system was not evaluated for its ability to
20 reproduce its thermal effect after various heating and
21 cooling cycles.

22 The aerospace industry has reported some
23 phase-change materials (inorganic salt hydrates such as
24 calcium chloride hexahydrate, lithium nitrate trihydrate,
25 zinc nitrate hexahydrate and polyethylene glycol with an
26 average molecular weight of 600) for uses in spacecraft

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1 (Hale, et al., "Phase Change Materials Handbook", NASA
2 Contractor Report CR-61363, Sept. 1971). These materials
3 have also been used in solar collectors and heat pumps in
4 residences (Carlsson, et al., Document D12:1978, Swedish
5 Council for Building Research). However, in these and
6 similar publications, the suitability of phase-change
7 materials for effective and prolonged heat storage and
8 release is influenced by the substrate in which they are
9 stored, its geometry and thickness, the effect of
10 impurities and the tendency of the phase-change materials
11 to supercool and exhibit reversible melting and
12 crystallization. Moreover, and perhaps the most
13 significant deficiency and limitation of the above
14 recommendations, is the fact that the phase-change
15 materials were recommended as incorporated into metal
16 containers, plastic pipes and other nonporous substrates
17 or very thick insulation such as wall board. No process
18 or suitable conditions for the incorporation of these
19 types of materials into hollow or non-hollow textile
20 fibers has been described. Therefore, the problem of
21 choosing a textile fiber and combining it with a
22 phase-change material in order to produce thermal storage
23 and release properties that could be retained for a
24 minimum of 5 heating and cooling cycles is an extremely
25 difficult one.

26 In addition to substances that store or release
27 thermal energy due to melting and/or crystallization
28 (phase-change materials) there is another class of
29 substances that are characterized by their high enthalpies
30 or thermal storage and release properties. These
31 substances are commonly called plastic crystals, and have
32 extremely high thermal storage or release values that
33 occur prior to and without melting, i.e., they have
34 thermal energy available without undergoing a change of
35 stage such as solid to liquid (melting) or liquid to solid

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(crystallization). Although the precise reasons why plastic crystals exhibit such unique thermal behavior prior to a change of state have not been verified, this thermal effect is believed to be due to a conformational and/or rotational disorder in these substances. Plastic crystal materials such as pentaerythritol and other polyhydric alcohols have been recommended for use in passive architectural solar designs and active solar dehumidifier or solar cooling systems (D. K. Benson, et al., Proc. Eleventh No. Am. Thermal Analysis Conf. 1981) because of their high thermal storage and release values that occur much below their melting point. However, as with the phase-change materials, no process or suitable conditions for the incorporation of these plastic crystals into hollow or non-hollow textile fibers has been described.

SUMMARY OF THE INVENTION

Temperature-adaptable textile fibers are provided which store heat when the temperature rises and release heat when the temperature decreases, in which phase-change or plastic crystalline materials are filled within hollow fibers, or impregnated upon non-hollow fibers.

The fibers are produced by dissolving the phase-change or plastic crystalline materials in a solvent such as water, thereafter filling the hollow fibers, or impregnating the non-hollow fibers, with the solution, followed by removal of the solvent. Alternatively, in the case of phase-change materials, the material may be applied to the fibers from a melt rather than solution.

The resultant product is a modified fiber which is temperature adaptable in both hot and cold environments for as many as 150 heating and cooling cycles, by releasing heat when the temperature drops, and storing heat when the temperature rises. As such, fabrics made

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1 from such fibers may be used to protect plants and
2 animals, may be incorporated in protective clothing, and
3 generally speaking may be employed in environments where
4 temperature fluctuations need to be minimized.

5 When polyethylene glycol is used as the impregnating
6 material, it is insolubilized on the fiber by
7 cross-linking, and the resultant product imparts valuable
8 properties to the fabric, in addition to thermal
9 properties, including the properties of soil release,
10 durable press, resistance to static charge, abrasion
11 resistance, pilling resistance and water absorbency.
12 Furthermore, polyethylene glycol may be impregnated on
13 cellulosic fibers other than textile fabrics, such as
14 paper and wood pulp fibers, for the purpose of imparting
15 the above properties thereto.

16 DESCRIPTION OF THE PREFERRED EMBODIMENTS

17 In the practice of the present invention the
18 phase-change or plastic crystalline materials which are to
19 be filled into such hollow fibers as rayon or
20 polypropylene, or impregnated into non-hollow fibers such
21 as cotton or rayon, first are dissolved in a solvent to
22 form a solution. Water is a suitable solvent in most
23 instances, although some materials are more readily
24 dissolved in alcohol such as ethyl alcohol or chlorinated
25 hydrocarbons such as carbon tetrachloride.

26 Wide ranges of solution concentrations are
27 suitable. The solution should not be too viscous that it
28 interferes with the ability of the solution to fill the
29 hollow fibers or to evenly impregnate the non-hollow
30 fibers, and it should not be too dilute that only minimal
31 amounts of material are deposited within or on the fibers.

32 Previously known techniques for filling hollow
33 fibers are suitable, such as taught in "Hollow Fibers -
34 Manufacture and Application", editor Jeanette Scott,

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1 published by Noyes Data Corp., 1981, and includes metering
2 the desired aqueous solution into the hollow fibers as
3 they are formed by extrusion during wet spinning.

4 As to impregnating non-hollow fibers, previously
5 known immersion and coating techniques for textile fibers
6 are suitable, such as techniques for finishing or dyeing,
7 or imparting fire-retardancy or wash-and-wear.

8 As a laboratory procedure for filling small numbers
9 of fibers, the following method may be employed: A
10 plurality of fibers are formed into a bundle. One end of
11 the bundle is immersed in solution, while the other end is
12 snugly inserted into an open end of a plastic or rubber
13 tube or hose which is connected to an aspirator, thereby
14 drawing solution into the fibers.

15 After the solution has filled the hollow fibers, or
16 has coated the non-hollow fibers, solvent is removed from
17 the solution to deposit the material within or upon the
18 fibers. Prior art solvent removal techniques in the
19 textile art are suitable, such as air drying or oven
20 drying. These techniques are well known in connection
21 with fabric finishing or dyeing, or imparting
22 flame-retardancy or wash-and-wear to textiles. In some
23 instances, the solvent can be removed by reduced pressure
24 or solvent extraction.

25 In the case of non-hollow fibers, a preliminary
26 solvent removal step may be included such as the use of
27 squeeze rollers to remove excess solvent prior to drying.
28 Such a preliminary step is well known in the textile
29 treatment art.

30 During the primary drying step, the temperature
31 preferably is maintained below the melting point of the
32 phase-change material or below the solid-to-solid
33 transition temperature of the plastic crystalline
34 material.

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1 After removal of solvent, in the case of hollow
2 fibers, the fiber ends may be sealed as taught in the
3 previously mentioned book on hollow fibers, and thereafter
4 the fibers may be formed into woven or nonwoven fabric.
5 With regard to impregnating non-hollow fibers, the step of
6 treating the fibers with solution of the phase-change or
7 plastic crystalline material preferably is carried out
8 after the fibers have already been formed into fabric.

9 As an alternative to dissolving the phase-change
10 material in a solvent prior to application to the fibers,
11 such materials may first be melted. Thereafter, the melt
12 itself is filled into or impregnated upon the fibers and
13 subsequently cooled for the purpose of resolidification.

14 Any phase-change or plastic crystalline material
15 which is chemically or physically compatible with the
16 fibers is suitable, which can be determined through
17 routine experimentation. The expression "chemically and
18 physically compatible", as used in the specification and
19 claims, means that the material does not react with the
20 fibers so as to lose its phase-change or transition
21 properties, is capable of being filled within the hollow
22 fiber, or impregnated upon the non-hollow fiber, and,
23 specifically with regard to phase-change materials, the
24 material must be able, in its liquid phase, to be retained
25 within the hollow fiber, or remain impregnated upon the
26 non-hollow fiber. The expression "phase-change material",
27 as used herein, refers to materials which transform from
28 solid to liquid and back, at a particular temperature; and
29 "plastic crystalline material" refers to material which
30 changes from one solid composition to another, and back,
31 at a particular temperature. It will be obvious that only
32 those materials whose temperature of phase change or
33 transition falls within a temperature of practical use for
34 the resultant fabric ordinarily should be employed in the
35 practice of the present invention, although, under special

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1 circumstances, it may be useful to employ a material whose
2 phase change or transition temperature falls outside this
3 normal range.

4 Preferably the phase-change materials are selected
5 from the group consisting of congruent inorganic salt
6 hydrates and polyethylene glycols, while the plastic
7 crystalline materials are polyhydric alcohols. More
8 particularly, the phase-change materials are selected from
9 the group consisting of calcium chloride hexahydrate in
10 admixture with strontium chloride hexahydrate, lithium
11 nitrate trihydrate and zinc nitrate hexahydrate,
12 polyethylene glycols having 5 to 56 monomer units with an
13 average molecular weight ranging from 300 to 3350.

14 The polyhydric alcohols preferably are selected from
15 the group consisting of pentaerythritol, 2,2-dimethyl-1,
16 3-propanediol, 2-hydroxymethyl-2-methyl-1,3-propanediol,
17 or amino alcohols such as 2-amino-2-methyl-1,
18 3-propanediol.

19 With regard to specific phase-change and plastic
20 crystalline materials, preferred concentrations (weight
21 percent of solution) in aqueous solutions for application
22 to fibers are as follows (in some cases the amount of
23 material which is deposited in or on specific types of
24 fibers, after solvent removal, also is given):

25 (a) 10--40% sodium sulfate decahydrate in
26 combination with 3-10% sodium borate decahydrate added to
27 prevent supercooling.

28 (b) 45-80% calcium chloride hexahydrate in
29 combination with 1-2.5% strontium chloride hexahydrate
30 added to prevent supercooling, 0.5-10.0 grams of material
31 deposited per gram of rayon or cotton fiber, and 0.4-1.6
32 grams per gram of polypropylene fiber.

33 (c) 80-95% zinc nitrate hexahydrate, 0.5-17.0 grams
34 deposited per gram of rayon or cotton, and 1.0 to 1.6
35 grams per gram of polypropylene.

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1 (d) 80-100% lithium nitrate trihydrate, 3-10 grams
2 deposited per gram of rayon or cotton, and 0.2-1.4 grams
3 per gram of polypropylene.

4 (e) 15-65% polyethylene glycol (300-3350 m.w.),
5 0.25-12.0 grams deposited per gram of rayon, cotton, wool,
6 polyester, polypropylene and so forth.

7 (f) 20-40% pentaerythritol, 1.0-2.0 grams deposited
8 per gram of rayon or cotton, and 0.4-0.8 grams per gram of
9 polypropylene.

10 (g) 40-60% 2-amino-2-methyl-1,3-propanediol,
11 0.4-2.8 grams deposited per gram of rayon or cotton, and
12 0.8-1.2 grams per gram of polypropylene.

13 (h) 40-60% 2,2-dimethyl 1-1,3-propanediol, 0.4-2.8
14 grams deposited per gram of rayon or cotton, and 0.7-1.1
15 grams per gram of polypropylene.

16 (i) 40-60% 2-hydroxymethyl-2-methyl-1,3-pro-
17 panediol, 0.5-5.0 grams per gram of rayon or cotton, and
18 0.6-1.0 grams per gram of polypropylene.

19 In the case of using polyethylene glycol as the
20 phase change material, especially on non-hollow fibers,
21 the material preferably is cross-linked on the fiber to
22 make it water insoluble, and thereby resistant to
23 laundering. While there are several cross-linking agents
24 known in the prior art for polyethylene glycol, those
25 having three or more reactive sites, e.g., 1,3-bis
26 (hydroxymethyl)-4,5-dihydroxyimidazolidinone-2, more
27 commonly known as dihydroxydimethylol ethylene urea
28 (DMDHEU), have been able to achieve the appropriate degree
29 of cross-linking at the necessary amount of add-on. For
30 instance, far more polyethylene glycol is placed on the
31 fiber in the practice of the present invention than was
32 previously done in the prior art of using polyethylene
33 glycol to impart durable press to fabrics; and, to date,
34 only the type of cross-linking agent as described above
35 has been able to achieve appropriate cross-linking at such

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1 a degree of add-on. Thus, only trifunctional or greater
2 functionality cross-linking agents are suitable. In
3 addition, such cross-linking is carried out by removal of
4 solvent and occurs by an ionic mechanism rather than by
5 free radical reactions promoted or caused by exposure of
6 the polyol to high energy radiation.

7 In the case of impregnating a non-hollow fiber,
8 such as cellulose, polyester, wool or other fiber, with
9 cross-linked polyethylene glycol, the preferred weight
10 percent of the solution is about 30-60% polyethylene
11 glycol (300-20,000 mw), and the add-on generally is from
12 0.15 to 1 grams per gram of fiber, preferably about
13 0.25-0.50 grams/gram. Below 0.25 grams/gram, add-on
14 usually is not sufficient to impart thermal storage and
15 release properties to the modified fibers, although other
16 above-enumerated properties still can be achieved.
17 Whatever the add-on, the degree of cross-linking is
18 important. Undercross-linking will not make the polymer
19 water insoluble. Overcross-linking destroys or negates
20 thermal activity, and also can adversely affect other
21 properties such as tensile and abrasion properties,
22 particularly of cellulosic fibers and/or cellulosic-
23 synthetic blends.

24 As to non-hollow cellulosic substrates, the
25 polyethylene glycol may be cross-linked in the above
26 amounts to non-textile materials such as paper and wood
27 pulp fibers for the purpose of enhancing the properties
28 thereof.

29 When cross-linking the polyethylene glycol, it is
30 important to impart a sufficient degree of cross-linking
31 so that the material is water insoluble. It is also
32 important to avoid too much cross-linking, which will
33 inhibit the material's ability to change phases. It has
34 been determined that the solution of the polyethylene
35 glycol preferably should contain, by weight, about 8-16%

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1 DMDHEU as the cross-linking agent, and 0.5-5.0% acid
2 catalyst, preferably mild catalysts such as magnesium
3 chloride/citric acid catalyst, sodium bisulfate,
4 p-toluenesulfonic acid or combinations of
5 p-toluenesulfonic acid with other acid catalysts, in
6 order to make the polyethylene glycol water insoluble,
7 and yet able to retain its ability to change phases upon
8 heating and cooling. With high molecular weight
9 polyethylene glycols, e.g., greater than 1500, specific
10 acid catalysts such as p-toluenesulfonic acid by itself
11 or in admixture with other acid catalysts such as $MgCl_2$
12 and citric acid, are necessary to insolubilize the polyol
13 onto the fiber and impart the desired properties.

14 Typical small scale operating conditions for pad
15 dry-cure and for applying cross-linked polyethylene
16 glycol to fibers include: a wet pick up of about
17 80-200%, drying at about 50-80°C for about 3-9 minutes,
18 and curing at about 100-170°C for about 0.5-5 minutes.
19 The ability to cure at lower temperatures, e.g., about
20 100-130°C, and yet still be able to fix the polymer so
21 that it doesn't wash off is advantageous.

22 It should be understood that the polyethylene
23 glycol is impregnated on the fibers and is not part of a
24 copolymer fiber structure. Nor is it present as an
25 additive for other materials impregnated on such fiber.
26 Still further, preferably it is unsubstituted, i.e., it
27 only has hydroxyl end groups.

28 Laundering studies show that the polyethylene
29 glycol-impregnated non-hollow fibers are durable for 50
30 launderings, that the beneficial thermal properties are
31 retained, and that pilling resistance is much better than
32 that of an untreated surface laundered the same number of
33 times.

34 The capabilities of phase-change materials in the
35 practice of the present invention varies from one
36 material to another. For example, many congruent

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1 inorganic salt hydrates exhibit a loss in thermal
2 effectiveness and a tendency to supercool after 50
3 heating and cooling cycles, whereas polyethylene glycol
4 does not do so up to 150 cycles. As another example,
5 sodium sulfate decahydrate in combination with sodium
6 borate decahydrate loses its effectiveness after 5
7 heating and cooling cycles. Likewise, there is a
8 variation among the plastic crystalline materials. For
9 example, pentaerythritol is only moderately effective
10 because it has a tendency to sublime from the fibers on
11 prolonged thermal cycling.

12 As a general rule, the plastic crystalline
13 materials are more advantageous than the phase-change
14 materials since the thermal storage and release effects
15 of the former are not dependent on melting and
16 crystallization, and often occur at temperatures much
17 below such melting or crystallization temperatures.
18 Modified fibers containing suitable plastic crystal
19 materials have little tendency to supercool or lose
20 thermal effectiveness on prolonged thermal cycling.

21 The hollow fibers preferably are rayon and
22 polypropylene of the single cavity type, but any hollow
23 fiber type such as polyester or polyamide, and hollow
24 fiber geometry such as multiple cavity are suitable. The
25 non-hollow fibers preferably are cotton, mercerized
26 cotton, rayon fibers, yarns and/or fabrics, but other
27 non-hollow fibers are suitable such as wool and
28 polyamides. With specific regard to polyethylene glycol
29 as the impregnating material for non-hollow fibers, the
30 substrate may be wood pulp, paper, a diverse group of
31 natural and/or synthetic fiber types, e.g., cellulose,
32 proteinaceous, polyester, polypropylene, polyamide,
33 glass, acrylic, blends of the preceding, and so forth.

34 Fibers with high moisture regain, i.e., 4% or
35 greater, such as rayon or cotton are preferred to fibers
36 such as polypropylene for incorporation of congruent
37 inorganic salt hydrates because rayon and cotton prolongs
38 the number of thermal cycles for which the modified

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1 fibers are thermally effective. That is, these
2 phase-change materials lose some water of hydration or
3 lose waters of hydration at a rate much faster than
4 rehydration after prolonged thermal cycling. Rayon and
5 cotton are superior to polypropylene in such situations
6 because (a) rayon and cotton have a greater affinity and
7 capacity for congruent inorganic salt hydrates and
8 provide initially higher thermal storage and release
9 values; and (b) they retain these desirable thermal
10 characteristics for a longer number of cycles because of
11 their ability to provide water from the fiber and thus
12 minimize or retard dehydration of the hydrates.

13 Hydrophilic fibers are superior to hydrophobic
14 fibers in many instances because the former have much
15 greater affinity for polyethylene glycol than the
16 latter. Presumably this is due to their hydrophilic
17 nature and ability to form hydrogen bonds with these
18 phase-change materials; and thus, fibers such as rayon or
19 cotton retain greater amounts of the polyethylene glycol.

20 The minimum length of the hollow fibers that are to
21 be filled generally should be about 10 mm, because
22 smaller fibers are difficult to handle. The preferred
23 length is at least 30 mm. There is no maximum length,
24 and thus continuous filaments can be filled with the
25 materials herein. Any non-hollow fiber length and
26 geometry may be modified by the present invention. The
27 process is suitable for treatment of woven and non-woven
28 yarns and fabrics or any other textile structure derived
29 from non-hollow fibers.

30 The thermal transfer properties of the product of
31 the present invention are illustrated in the following
32 examples.

33 EXAMPLE 1

34 Incorporation of Polyethylene Glycol
35 (av. molecular wt. of 600) into
36 Hollow Rayon Fibers

37 Hollow rayon fibers (38 mm in length) were tied

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1 into a parallel fiber bundle, tightly aligned inside an
2 O-ring in a vertical position, and a 57% aq. solution of
3 polyethylene glycol with an average molecular weight of
4 600 (Carbowax 600) aspirated through the fibers under
5 reduced pressure for 30 minutes or until the solution was
6 visually observed to be at the top of the fiber. The
7 modified fibers were then cooled at -15°C for 1 hour and
8 dried at 18°C for 24 hours to remove excess water and
9 cause the phase-change material to solidify. Excess
10 solid on the exterior of the fiber was removed, then the
11 fiber was conditioned at 25°C/45% RH in a dessicator
12 containing KNO₂ to produce a modified fiber containing on
13 a weight/weight basis, 7.0 grams of Carbowax 600 per gram
14 of rayon fiber. The modified fibers were then evaluated
15 for up to 150 heating and cooling cycles at -40 to +60°C
16 for their ability to store and release thermal energy by
17 differential scanning calorimetry. At 1 heating and
18 cooling cycle, the thermal energy available for storage
19 on increasing temperature was 39.1 calories/gram in the
20 temperature interval of -3 to +37°C and the thermal
21 energy available for release on decreasing temperature
22 42.6 calories/gram in the temperature interval of -23 to
23 17°C.

24 After 150 thermal cycles, the thermal energy
25 available for storage was 41.9 calories/gram and for
26 releast 41.0 calories/gram for the same temperature
27 intervals.

28 In contrast, unmodified hollow rayon fibers after 1
29 heating and cooling cycle exhibited fairly linear
30 behavior and had in the same temperature ranges, thermal
31 storage values of 16.2 calories/gram and release values
32 of 14.9 calories/gram due only to the specific heat of
33 the unmodified fiber.

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EXAMPLE 2

Incorporation of Polyethylene Glycol
(av. molecular wt. of 600) into Hollow
Polypropylene Fibers

Hollow polypropylene fibers (135 mm in length) were prepared and treated as in Example 1 with a 57% aqueous solution of polyethylene glycol (Carbowax 600), cooled, dried and conditioned, as in Example 1, to produce a modified fiber containing 1.2 grams of Carbowax 600 per gram of polypropylene fiber. When the modified hollow fibers were evaluated by thermal analysis for up to 50 heating and cooling cycles at -40 to +60°C, their thermal energy available for storage after 1 heating and cooling cycle was 32.3 calories/gram in the temperature interval of -3 to +37°C (increasing temperature) and for release 31.5 calories/gram in the temperature interval of -23 to +17°C (decreasing temperature). After 50 thermal cycles, thermal energy for storage in the modified fibers was 35.2 calories/gram and for release 26.9 calories/gram at the same temperature intervals for heating and cooling.

In contrast, unmodified hollow polypropylene fibers after 1 heating and cooling cycle exhibited fairly linear behavior and had in the same temperature intervals, thermal storage values of 16.9 calories/gram and release values of 15.4 calories/gram, due to only the specific heat of the unmodified fibers.

EXAMPLE 3

Incorporation of Polyethylene Glycol
(av. molecular wt. of 3350) into Hollow
Polypropylene Fibers

Hollow polypropylene fibers were treated as in Example 2 with a 57.2% aqueous solution of polyethylene

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glycol (Carbowax 3350), cooled, dried, and conditioned, as in Example 1, to produce a modified fiber containing 1.0 gram of Carbowax 3350 per gram of polypropylene fiber. When the modified hollow fibers were evaluated by thermal analysis for up to 50 heating and cooling cycles at -40 to +80°C, their thermal energy available for storage after 1 heating and cooling cycle was 35.6 calories/gram in the temperature interval 42 to 77°C (increasing temperature) and for release 33.5 calories/gram in the temperature interval of 17 to 52°C (decreasing temperature). After 50 thermal cycles, thermal energy for storage in the modified fibers was 32.8 calories/gram and for release 34.3 calories/gram at the same temperature intervals for heating and cooling.

EXAMPLE 4

Incorporation of Polyethylene Glycol (av. molecular wt. of 3350) into Hollow Rayon Fibers

Hollow rayon fibers were treated with the same concentration of Carbowax 3350 as in Example 3, cooled, dried, and conditioned, as in Example 1, to produce a modified fiber containing 11.3 grams of Carbowax 3350 per gram of rayon fiber. Evaluation of the modified hollow fibers by calorimetry for up to 50 heating and cooling cycles at -40 to +80°C, indicated that their thermal energy available for storage after 1 heating and cooling cycle was 43.5 calories/gram in the temperature interval of 42 to 77°C and for release 49.6 calories/gram in the temperature interval of 17 to 52°C. After 50 thermal cycles at the same temperature intervals, thermal energy for storage in the modified fibers was 43.3 calories/gram and for release 47.1 calories/gram.

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EXAMPLE 5

Incorporation of Polyethylene Glycol
(av. molecular wt. 1000) into Hollow
Rayon Fibers

A 57.4% aqueous solution of polyethylene glycol (Carbowax 1000) was aspirated through hollow rayon fibers under reduced pressure, cooled, dried, and conditioned, as in Example 1, to produce a modified hollow fiber containing 10.8 grams of Carbowax 1000 per gram of rayon fiber. When the modified fibers were evaluated by calorimetry for up to 50 thermal cycles at -40 to +60°C their thermal energy available for storage after 1 heating cycle was 43.2 calories/gram in the temperature interval of 17 to 52°C and for release after 1 cooling cycle 41.8 calories/gram in the temperature interval of -3 to 32°C. After 50 thermal cycles, thermal energy for storage in the modified fibers was 43.5 calories/gram and for release 41.6 calories/gram at the same temperature intervals for heating and cooling.

EXAMPLE 6

Incorporation of Polyethylene Glycol
(av. molecular wt. 400) into Hollow
Polypropylene Fibers

A 57.1% solution of polyethylene glycol (Carbowax 400) was aspirated through hollow polypropylene fibers under reduced pressure, cooled, dried, and conditioned, as in Example 1, to produce a modified hollow fiber containing 1.2 grams of Carbowax 400 per gram of polypropylene fiber. Evaluation of the modified fibers by calorimetry for up to 10 heating and cooling cycles at -40 to +60°C indicated thermal storage values of 28.5 calories/gram (temperature interval: -28 to +12°C)

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1 and release values of 24.9 calories/gram (temperature
2 interval: -48 to -8°C) after 1 heating and cooling cycle,
3 respectively. After 10 thermal cycles, the thermal
4 storage and release values at the same temperature
5 intervals were respectively 28.1 calories/gram and 25.7
6 calories/gram.

7 EXAMPLE 7

8 Incorporation of Polyethylene Glycol
9 (av. molecular wt. of 600) into
10 Cotton Fabric

11 100% desized, scoured, and bleached cotton
12 printcloth (3.15 oz/yd²; thread count 84 warp x 76 fill;
13 1 ft. wide x 9 ft. long) was immersed in a 50% aqueous
14 solution of polyethylene glycol (Carbowax 600) at 25°C,
15 then excess solution removed by running the treated
16 fabric through a squeeze roller to a wet pickup of 100%.
17 Two one ft.² samples were removed from the treated
18 fabric, one of which was placed on a flat surface and
19 allowed to air-dry overnight for 24 hours at 15°C, and
20 the other dried for 85 seconds at 75°C in a Mathis
21 Laboratory Dryer (one that stimulates commercial drying
22 without liquid migration). The drying procedure is to
23 effect solidification of the phase-change material on the
24 fabric. After drying, each treated fabric was
25 conditioned, as described as in Example 1, to give a
26 modified fabric containing 0.6 grams of Carbowax 600 per
27 gram of cotton fabric. When the modified cotton fabrics
28 were evaluated by thermal analysis at -23 to +37°C, their
29 thermal energy available for storage was 18-20 calories
30 per gram for 1 or 10 heating cycles, with little
31 difference in these values for fabrics dried by each
32 method. Similar results were obtained for thermal energy
33 available for release (16-18 calories per gram for 1 or
34 10 cooling cycles). In contrast, the unmodified cotton
35 fabric had thermal storage values of 11-12

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calories per gram and release values of 10.5-11.8 calories per gram in the same temperature intervals, due only to the specific heat of the unmodified fibers.

EXAMPLE 8

Incorporation of $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ into Hollow Rayon Fibers

Pure $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ was melted at 30°C , then aspirated under reduced pressure into hollow rayon fibers that were subsequently cooled, dried, and conditioned, as in Example 1, to produce a modified hollow fiber containing 9.5 grams of lithium nitrate trihydrate per gram of rayon fiber. The modified fibers were then evaluated up to 50 thermal cycles at -40 to $+60^\circ\text{C}$. Their thermal energy available for storage after 1, 10, and 50 heating cycles was respectively 72.4, 74.7 and 37.4 calories/gram, and for thermal release after 1, 10, and 50 cooling cycles, 53.1, 42.2, and 9.8 calories/gram, with progressive supercooling occurring by 50 cycles. Temperature intervals for all heating cycles for measuring thermal storage were 17 to 42°C , while the temperature interval chosen for cooling cycles varied, and was -1 to 9°C , -7 to $+2^\circ\text{C}$, and -22 to 17°C for 1, 10 and 50 cooling cycles, respectively.

Although the rayon/lithium nitrate trihydrate system lost its thermal effectiveness on prolonged cycling, it was superior to either the pure $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ alone or to this phase change material incorporated into the polypropylene hollow fiber. After 1 and 10 cycles thermal storage values for the pure $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ were 65.8 and 23.0 calories/gram (1 and 10 cycles) thermal storage values for the pure $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ were 65.8 and 23.0 calories/gram (1 and 10 cycles) and 30.5 and 22.1 calories/gram (1 and 10 cycles) for the lithium

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nitrate trihydrate incorporated into the polypropylene fiber at a ratio of 1.9 grams/gram of fiber after cooling, drying and conditioning. On cooling, similar trends were observed. After 1 and 10 cooling cycles, the pure $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ had thermal storage values of 50.0 and 2.3 calories/gram and the $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ treated fibers corresponding values of 4.7 and 0.2 calories/gram, the latter due only to the specific heat of the polypropylene fiber. Temperature values varied, particularly with cooling cycles, and generally were measured at intervals reflecting the peak temperature midpoint of crystallization on cooling.

EXAMPLE 9

Incorporation of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ into Hollow Rayon Fibers

An 89.7% aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was incorporated into hollow rayon fibers (38 mm in length) that were cooled, dried, and conditioned, as in Example 1, to produce a modified fiber with 15.0 grams of zinc nitrate hexahydrate per gram of rayon fiber. When the modified fiber was evaluated between -40 to $+60^\circ\text{C}$ by differential scanning calorimetry, it produced 28.6 calories per gram for thermal storage (temperature interval: 22 to 46.6°C), and 16.9 calories/gram for thermal release (temperature interval: -3 to 9°C) after 1 cycle. After 5 thermal cycles, the corresponding thermal storage and release values were 36.6 calories/gram on heating (same temperature interval as 1 heating cycle) and 12.9 calories/gram on cooling (temperature interval: -3 to $+9^\circ\text{C}$).

When the same concentration of the above phase-change material was incorporated into hollow polypropylene fibers, the modified fibers contained 1.4 grams of zinc nitrate hexahydrate per gram of polypropylene. On their evaluation by calorimetry, their

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thermal storage values for the 1 and 5 heating cycles were respectively, 23.3 and 24.9 calories/gram (temperature interval: 22 to 48°C) and for thermal release after 1 and 5 cycles, 8.2 and 5.7 calories/gram (temperature interval: 12 to 20°C), with the latter value due only to the specific heat of the polypropylene fiber.

EXAMPLE 10

Incorporation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ / $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ into Hollow Rayon Fibers

A 49.4% $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ / 1.00% $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ aqueous solution was aspirated through hollow rayon fibers that were dried, cooled, and conditioned, as in Example 1, to produce a modified fiber containing 3.2 grams of calcium chloride hexahydrate/ strontium chloride hexahydrate per gram of rayon fiber. When the modified fiber was evaluated by calorimetry at -40 to +60°C, it had thermal storage values of 11 calories/gram (temperature interval: 22 to 37°C) and release values of 14 calories/gram (temperature interval: -8 to +17°C) after 1 thermal cycle. After 10 heating and cooling cycles, its thermal storage value was 17 calories/gram and release value 16 calories/gram (same temperature interval as 1 cycle).

EXAMPLE 11

Incorporation of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ / $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ into Hollow Rayon Fibers

A 40% $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ / 10% $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ aqueous solution was aspirated through hollow rayon fibers that were dried, cooled and conditioned, as in Example 1, to produce a modified fiber containing

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0.1 gram of sodium sulfate hexahydrate/borax per gram of rayon fiber. When the modified fiber was evaluated by calorimetry at -40 to +60°C, it was practically indistinguishable from unmodified hollow rayon fibers in its thermal storage and release properties after 5 heating and cooling cycles, and exhibited no pronounced endotherms or exotherms (associated with storage and release effects) even after only 1 heating and cooling cycle. Consequently, all phase-change materials do not work.

EXAMPLE 12

Incorporation of 2,2-Dimethyl-1,3-propanediol into Hollow Rayon Fibers

Hollow rayon fibers cut from tow (135 mm in length) were prepared and treated, as in Example 1, with a 50% aqueous solution of 2,2-dimethyl-1,3-propanediol (DMP), cooled, dried and conditioned as in Example 1 to produce a modified fiber containing 2.8 grams of DMP per gram of rayon fiber. When the modified hollow fibers were evaluated by thermal analysis for up to 50 heating and cooling cycles at 7 to 62°C, their thermal energy available for storage after 1 heating and cooling cycle was 30.5 calories/gram in the temperature interval of 32 to 62°C (increasing temperature) and for release 27.2 calories/gram in the temperature interval of 37 to 7°C (decreasing temperature). After 50 thermal cycles, thermal energy for storage in the modified rayon fibers was 29.5 calories/gram and for release 26.4 calories/gram at the same temperature intervals for heating and cooling. In contrast, unmodified hollow rayon fibers after 1 heating and cooling cycle exhibited fairly linear behavior and had in the same temperature intervals, thermal storage values of 9.3 calories/gram and release values of 8.7 calories/gram, due to only the specific heat of the unmodified fibers.

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EXAMPLE 13Incorporation of 2,2-Dimethyl-1,3-propanediol
into Cotton Fabric

100% desized, scoured, and bleached cotton printcloth (3.15 oz/yd²; thread count 84 warp x 76 fill; 1 ft. wide x 9 ft. long) was immersed in a 50% aqueous solution of DMP, then excess solution removed from the fabric by running the treated fabric through a squeeze rolled to a wet pickup of 100%. Two 1 ft² samples were removed from the treated fabric, one of which was placed on a flat surface and allowed to air-dry overnight for 24 hours at 15°C, and the other dried for 85 seconds at 75°C in a Mathis Laboratory Dryer (one that simulates commercial drying without liquid migration). The drying procedure is to effect solidification of the phase-change material on the fabric. After drying, each treated fabric was conditioned as described in Example 1 to give a modified fabric containing 0.6 grams of DMP per gram of cotton fabric. When these modified fabrics were evaluated by thermal analysis at 7 to 62°C, their thermal energy available for storage was 18-21 calories/gram for 1 or 10 heating cycles, with little difference in these values for fabrics dried by each method. Similar results were obtained for thermal energy available for release (16-18 calories/gram for 1 or 10 cooling cycles). In contrast, the unmodified cotton fabric had thermal storage values of 8.6-9.1 calories/gram and release values of 7.9-8.1 calories/gram in the same temperature intervals, due only to the specific heat of the unmodified fibers.

EXAMPLE 14Treatment of Non-hollow Rayon Fibers with
2,2-Dimethyl-1,3-propanediol

Staple rayon fibers (as two-ply yarn, 32-50 mm

- 23 -

1 staple length; 30.7 mg/m denier) were immersed in excess
2 50% aqueous DMP solution, centrifuged for 5 minutes at
3 2080 rpm to remove excess DMP, cooled, dried and
4 conditioned, as in Example 12, to produce a modified
5 fiber containing 0.4 grams of DMP per gram of rayon
6 fiber. When the treated rayon fibers were evaluated by
7 thermal analysis for up to 50 heating and cooling cycles
8 at 7 to 62°C, their thermal energy for storage after 1
9 heating and cooling cycle was 15.3 calories/gram in the
10 temperature interval 32 to 62°C (increasing temperature)
11 and for release 12.4 calories/gram in the temperature
12 interval of 37 to 7°C (decreasing temperature). After 50
13 thermal cycles, thermal energy for storage of the treated
14 rayon fibers was 12.5 calories/gram and for release 11.2
15 calories/gram at the same temperature intervals for
16 heating and cooling.

17 EXAMPLE 15

18 Incorporation of 19 2-Hydroxymethyl-2-methyl-1,3-propanediol 20 into Hollow Polypropylene Fibers

21 Hollow polypropylene fibers were treated, as in
22 Example 12, with a 50% aqueous solution of
23 2-hydroxymethyl-2-methyl-1,3-propanediol (HMP), cooled,
24 dried and conditioned as above to produce a modified
25 fiber containing 0.8 grams of HMP per gram of
26 polypropylene fiber. When the modified hollow fibers
27 were evaluated by thermal analysis for up to 50 heating
28 and cooling cycles at 47 to 102°C, their thermal energy
29 available for storage after 1 heating and cooling cycle
30 was 32.7 calories/gram in the temperature interval of 72
31 to 102°C (increasing temperature) and for release 28.8
32 calories/gram in the temperature interval of 77 to 47°C
33 (decreasing temperature). After 50 thermal cycles,
34 thermal energy for storage in the modified fibers was
35 31.7 calories/gram and for release 28.4 calories/gram at
36 the same temperature intervals for heating and cooling.

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EXAMPLE 16Treatment of Cotton Fibers with
2-Hydroxymethyl-2-methyl-1,3-propanediol

Cotton fibers (as mercerized sewing thread-three plied, 23-32 mm staple length and a denier of 31.8 mg/m) were immersed in excess 50% aqueous HMP solution, centrifuged for 5 minutes at 2080 rpm to remove excess HMP, cooled, dried and conditioned as in Example 12 to produce a modified fiber containing 0.7 grams of HMP per gram of cotton fiber. When the treated cotton fibers were evaluated by thermal analysis for up to 50 heating and cooling cycles at 47 to 102°C, their thermal energy for storage after 1 heating and cooling cycle was 27.5 calories/gram in the temperature interval 72 to 102°C (increasing temperature) and for release 23.4 calories/gram in the temperature interval of 77 to 47°C (decreasing temperature). After 50 thermal cycles, thermal energy for storage of the treated cotton fibers was 25.3 calories/gram and for release 23.2 calories/gram at the same temperature intervals for heating and cooling. In contrast, untreated cotton fibers after 1 heating and cooling cycle exhibited fairly linear behavior and had in the same temperature intervals, thermal storage values of 10.0 calories/gram and release values of 8.9 calories/gram due to the specific heat of the unmodified fibers.

EXAMPLE 17Treatment of Cotton Fibers with
2-Amino-2-methyl-1,3-propanediol

Cotton fibers (as mercerized sewing thread-three plied 25-32 mm staple length and a denier of 31.8 mg/m) were immersed in excess 50% aqueous 2-amino-2-methyl-1,3-propanediol (AMP), excess AMP

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1 removed and the fibers cooled, dried and conditioned as
2 in Example 16 to produce modified cotton fibers
3 containing 1.1 grams of AMP per gram of cotton fiber.
4 When the treated cotton fibers were evaluated by thermal
5 analysis for up to 50 heating and cooling cycles at -3 to
6 102°C, their thermal energy for storage after 1 heating
7 and cooling cycle was 37.8 calories/gram in the
8 temperature interval 72 to 102°C (increasing temperature)
9 and for release 20.0 calories/gram in the temperature
10 interval of 92 to 52°C (decreasing temperature). After
11 50 thermal cycles, thermal energy for storage of the
12 treated cotton fibers was 30.2 calories/gram and for
13 release 18.6 calories/gram at the same temperature
14 intervals for heating and cooling.

15 EXAMPLE 18

16 Incorporation of Pentaerythritol into 17 Hollow Rayon Fibers

18 Hollow rayon fibers cut from tow (135 mm in length)
19 were prepared and treated, as in Example 12, with a 30%
20 aqueous solution of pentaerythritol (PET), cooled, dried
21 and conditioned, as in Example 12, to produce a modified
22 fiber containing 1.2 grams of PET per gram of hollow
23 rayon fiber. When the modified hollow fibers were
24 evaluated by thermal analysis for up to 10 heating and
25 cooling cycles at 152 to 207°C, their thermal energy
26 available for storage after 1 heating and cooling cycle
27 was 39.5 calories/gram in the temperature interval of 177
28 to 207°C (increasing temperature) and for release 34.0
29 calories/gram in the temperature interval of 182 to 152°C
30 (decreasing temperature). After 50 thermal cycles,
31 thermal energy for storage and release in the modified
32 hollow rayon fibers was indistinguishable from the
33 untreated hollow rayon fibers.

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EXAMPLE 19

Incorporation of Polyethylene Glycol
(av. molecular wt. 600) into Cotton Fabric by its
Reaction with Crosslinking Agent

100% desized, scoured and bleached cotton printcloth (3.7 oz/yd²; thread count 80 warp x 80 fill; 10 in. wide x 24 in. long) was immersed in an aqueous solution containing by weight 50% polyethylene glycol (Carbowax 600), 10% dihydroxydimethylol-ethylene urea (DMDHEU) 3% mixed catalyst (MgCl₂/citric acid) at 25°C, then excess solution removed by running the treated fabric through a squeeze roller at 50 lb. pressure to a wet pickup of 100%. The fabric was then mounted on a pin frame, dried 7 min. at 60°C in a force-draft oven, then cured an additional 3 min. at 160°C. The treated fabric was subsequently given a conventional machine laundering and tumble drying (warm/cold cycle for 10 min. with commercial phosphate detergent and dried for 15 mins. on normal drying cycle) or alternatively washed for 20 mins. at 50°C with running tap water and liquid detergent prior to tumble drying. The resultant fabric had a weight gain or add-on of 40.0% (0.4 gms. per gram of fiber). If the crosslinking agent were not employed, the polyethylene glycol would readily wash off on exposure to excess water. The modified fabric was conditioned at standard atmospheric conditions (65% RH/70°F), and evaluated by thermal analysis at -3 to +37°C. It had thermal energy available for storage of 16.4 calories per gram for 1 or 10 heating cycles, with little difference in these values after the initial cycle. Similar results were obtained for thermal energy available for release at -17 to +23°C (14.9 calories per gram for 1 or 10 cooling cycles). In contrast, the unmodified cotton had thermal storage values of 9.6 calories per gram and

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1 release values of 9.7 calories per gram in the same
2 temperature intervals, due only to the specific heat of
3 the unmodified fabric.

4 EXAMPLE 20

5 Attempts to Incorporate Polyethylene Glycol into
6 Cotton Fabric Using Other Crosslinking Agents

7 Cotton printcloth (as in Example 19) was padded
8 with 50% aqueous polyethylene glycol (Carbowax 1,000)
9 containing 3% magnesium chloride/citric acid as the
10 catalyst with the following crosslinking agents: with
11 (a) 10% formaldehyde; (b) 10% diisopropyl carbamate; and
12 (c) 10% dimethylolethylene urea (DMEU). In each instance
13 the fabrics were treated (dried and cured) as in Example
14 1A, but little reaction took place between the
15 polyethylene glycol and these crosslinking agents as
16 evidenced by the very low add-ons (3-5% or 0.03-0.05 gm
17 per gram of fiber). Thermal analyses of these fabrics
18 showed them to essentially be no different than the
19 untreated cotton fabrics with regard to their thermal
20 storage and release fabric properties, with their heat
21 content due only to the specific heat of the fiber.

22 EXAMPLE 21

23 Attempts to Incorporate Higher Molecular
24 Weight Polyethylene Glycols into Cotton Fabrics

25 Cotton printcloth (as in Example 19) was padded
26 with various concentrations of aqueous polyethylene
27 glycols (M.W. 3,350 and M.W. 8,000), DMDHEU and a
28 magnesium chloride/citric acid catalyst (30% by wt. of
29 the crosslinking agent). The following combinations were
30 used: 30-50% aqueous polyethylene glycol (av. mol. wt.
31 8,000), 10% DMDHEU, 3% magnesium chloride/citric acid
32 catalyst, 50% aqueous polyethylene glycol (av. mol. wt.

- 28 -

3,350), 10 to 15% DMDHEU, 3.0 to 4.5% magnesium chloride/citric acid catalyst. In each instance, the fabric was treated (dried and cured) as in Example 19, but only moderate weight gains were achieved (8-17% or 0.08-0.17 gm per gram of fiber) after laundering, indicating that not enough reaction had taken place to insolubilize the polymers. In all instances, the modified fabrics were essentially unchanged in their thermal storage and release characteristics, i.e., the same as the unmodified cotton fabrics from which they were derived.

EXAMPLE 22

Incorporation of Polyethylene Glycol (Average Molecular Weight 1,000) into Wool and into Polyester Fabrics by its Reaction with Crosslinking Agents

Worsted wool fabric (5.4 oz/yd²; thread count 55 warp x 45 fill; 10 in. wide x 10 in. long) was immersed in an aqueous solution containing by weight 50% polyethylene glycol (Carbowax 1000), 12% dihydroxydimethylethylene urea (DMDHEU), 3.6% mixed catalyst (MgCl₂/citric acid) at 25°C, then excess solution removing by running the treated fabric through a squeeze roller at 50 lb. pressure to a wet pickup of 94%. The fabric was dried, cured and given 1 laundering as in Example 19, and had an add-on or weight gain of 48.0% (0.48 gm per gram of fiber) after drying and conditioning. As previously indicated, the polyethylene glycol will wash off readily in water if it is not crosslinked. The resultant fabric was evaluated by thermal analysis at -3 to +37°C, and had thermal energy available for storage of 19.5 calories per gram for 1 or 10 heating cycles, with little difference in these values after the initial cycle. Similar results were obtained for thermal energy available for release at +17 to -23°C (16.3 calories per gram for 1 or 10

- 29 -

cooling cycles). In contrast, the unmodified wool had thermal storage values of 12.5 calories per gram and release values of 12.8 calories per gram in the same temperature intervals, due only to the specific heat of the unmodified fabric.

Treatment of heat set polyester fabric (3.6 oz/yd²; thread count 67 warp x 57 fill; 10 in. wide x 10 in. long) under identical conditions as that for the wool above (only difference was a 77% wet pickup), produced a modified fabric with a weight gain of 42.9% (0.429 gm per gram of fiber) that had thermal storage values of 12.7 calories/gram for 1 or 10 heating cycles and thermal release values of 13.1 calories/gram for 1 or 10 cooling cycles (same ranges as the wool fabrics). In contrast, the unmodified polyester had thermal storage values of 9.3 calories/gram and thermal release values of 9.7 calories/gram for 1 or 10 cycles due only to the specific heat of the unmodified fabric.

EXAMPLE 23

Incorporation of Polyethylene Glycol (av. mol. wt. 600) into Cotton Fabrics by its Reaction with Crosslinking Agents to Produce Modified Fabrics Having Improved
(Except Thermal Storage and Release) Properties

Cotton printcloth (as in Example 19) was immersed separately into two different aqueous solutions (by wt.) of Carbowax 600; (a) 35% polyethylene glycol, 7% dihydroxydimethylolethylene urea (DMDHEU), 2.1% mixed catalyst (MgCl₂/citric acid); and (b) 50% polyethylene glycol, 15% DMDHEU, and 4.5% mixed catalyst (MgCl₂/citric acid) at 25°C, then excess solution removed by running each of the treated fabrics through a squeeze roller at 40 lb. pressure to a wet pickup of 100%. Fabrics were then mounted on pin frames, dried 7 min. at 60°C in a force-draft oven, then cured an additional 2 min. at 170°C. Both fabrics were washed

- 30 -

for 20 mins. at 50°C with running tap water and liquid detergent prior to tumble drying. After conditioning, the first fabric had a weight of 16.5% while the second fabric had a weight gain of 59%. Neither of the fabrics exhibited any endotherms or exotherms on heating or cooling cycles when evaluated by differential scanning calorimetry and were essentially the same as the untreated cotton fabrics in their thermal storage and release properties; i.e., their heat content was due only to their specific heat. However, other textile properties in both treated fabrics were improved relative to untreated cotton printcloth: (a) conditioned wrinkle recovery (warp + fill) angle in the first treated fabric was 292° and 278° in the second treated fabric compared to only 170° for untreated cotton fabric; (b) oily soil release (using a modified Milliken Test Method DMRC-TT-100 in which the fabrics were soiled then washed and their reflectances values measured) was improved for both treated fabrics (retention of 90 and 86% of their reflectance for the first and second treated fabrics) relative to the control (only 54% retention of reflectance); (c) static charge remaining on the treated fabrics at 65% relative humidity (AATCC Test 76-1982) was 11,000 and 2,000 (ohms $\times 10^8$ compared to 91,000 for the untreated cotton printcloth).

EXAMPLE 24

Incorporation of Polyethylene Glycol
(av. mol. wt. 1,450) into Acrylic Fabric by its
Reaction with Crosslinking Agents

Acrylic fleece fabric (5.2 oz/yd²; 18 in x 24 in) was immersed in an aqueous solution containing 50% aq. polyethylene glycol 1,450, 13% DMDHEU, 3.9% mixed catalyst (MgCl₂/citric acid) at 25°C, then excess solution removed as in Example 23 (40 lb. pressure) to give a fabric with a wet pickup of 166%. The fabric was

- 31 -

1 subsequently dried on a pin frame for 6 min. at 80°C,
2 then cured for 2 min. at 140°C. The modified fabric was
3 then washed and tumble dried (as in Example 19) to give
4 an add-on or weight gain of 87%. The resultant fabric
5 had thermal storage values of 19.8 cal/g in the range of
6 +2 to +42°C on heating and thermal release values of 20.2
7 cal/g in the range of +27 to -13°C on cooling,
8 characterized by an endotherm on heating and an exotherm
9 on cooling. In contrast the untreated acrylic fabric has
10 thermal storage values of only 11.0 cal/g and thermal
11 release values of 9.6 cal/g in the same temperature
12 ranges.

13 The modified acrylic fabric also possessed superior
14 flex abrasion compared to the untreated acrylic fabric.
15 When the Stoll flex abrasion of the back sides of both
16 fabrics were measured, the treated fabric lasted 4,650
17 cycles to failure while the untreated fabric lasted only
18 792 cycles. Residual static charge (tested as in Example
19 23) was also substantially less for the treated fabric
20 (10,070 x 10⁸ ohms) than for untreated fabric (57,000 x
21 10⁸ ohms).

22 EXAMPLE 25

23 Incorporation of Polyethylene Glycol
24 (av. molecular wt. 1,000)
25 into Single Knit Jersey T-Shirts
26 (50/50 Cotton/Polyester)

27 by Reaction with Crosslinking Agents and Evaluation
28 of Durability of Finish to Prolonged Laundering

29 50/50 cotton/polyester (light blue color) single
30 knit jersey T-shirts (4.4 oz/yd² were immersed in 50% aq.
31 PEG-1,000/11% DMDHEU/3.3% mixed catalyst (MgCl₂/ citric
32 acid) at 25°C, excess solution removed at 40 lb. pressure
33 (as in Example 23) to a wet pickup of 100%. The shirts
34 were draped over pin frames and dried and cured as in
35 previous examples (dried 7 min. at 75°C

- 32 -

1 and cured 2 min. at 150°C). The shirts were machine
2 washed and tumble dried to give modified garments with
3 weight gains of 55% after conditioning. The thermal
4 storage and release values of the treated shirt were on
5 heating (in the range of -3 to +37°C) 15.6 cal/g and on
6 cooling (in the range of -17 to +23°C) 14.7 cal/g,
7 compared to only 9.8 cal/g and 9.7 cal/g on heating and
8 cooling for untreated shirts laundered and dried once.

9 After 50 machine washings and tumble dryings, the
10 treated shirts still had a weight gain of 37%, and had
11 little if any pilling or surface entanglement of fibers
12 compared to extensive and visually noticeable pilling in
13 untreated shirts that were also laundered and dried 50
14 times. Moreover, the thermal storage and release
15 properties of the treated shirts after 50 launderings
16 were respectively 13.7 cal/g and 13.5 cal/g on heating
17 and cooling in the same temperatures ranges described
18 above. These values were significantly higher than those
19 of untreated shirts laundered 50 times (9.5 cal/g on
20 heating and 9.5 cal/g on cooling) in the same temperature
21 intervals.

22 EXAMPLE 26

23 Incorporation of Polyethylene Glycol
24 (av. molecular wt. 1,000)
25 into Glass Fabric by its
26 Reaction with Crosslinking Agents

27 Fiberglas fabric (3.2 oz/yd²) was treated
28 identically as the T-shirts in Example 25 to a wet pickup
29 of 50%, dried 7 min. at 60°C and cured 3 min. at 160°C,
30 washed in warm water and detergent for 30 min. and
31 air-dried. After conditioning, the treated glass fabric
32 had a weight gain of 21%. Its moisture regain after 12
33 hours was appreciably higher (8.2%) than the untreated
34 glass fabric (0.4%) using standard test methods for this
35 evaluation. Its thermal storage in the range of

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-3 to +37°C was 14.3 cal/g on heating and characterized by an endotherm in this range in contrast to the untreated glass fabric whose thermal storage value was only 5.5 cal/g in the same range and due only to the specific heat of the glass fiber or fabric.

EXAMPLE 27

Incorporation of Polyethylene Glycol (av. molecular wt. 1,000) into Cotton/Polyester Fabric by its Reaction with Crosslinking Agents at Low Cure Temperatures

50/50 cotton/polyester printcloth (4.1 oz/yd²) was treated identically as were the T-shirts in Example 25 at 40 lb. pressure to a wet pickup of 100%. The fabric was subsequently dried 7 min. at 75°C and dried at a low cure temperature of only 110°C for 2 min., then machine washed and tumble dried to a wt. gain of 45% after conditioning. The resultant fabric had a thermal storage value (on heating) of 18.7 cal/g in the range of +7 to +47°C and a thermal release value (on cooling) of 16.8 cal/g in the range of +17 to -23°C. For untreated cotton/polyester printcloth in the same temperature intervals, the thermal storage and release values (due to specific heat of the fiber alone) were respectively on heating 10.1 cal/g and on cooling 9.7 cal/g. Moreover, the treated fabric had improvement in several properties relative to the untreated fabric: (a) flex abrasion-cycles to failure (>5,000 for treated vs. 3,500 for untreated); (b) pilling resistance rating with brush pilling apparatus (5.0 for treated vs. 3.3 for untreated, with 5.0 being the best rating); (c) conditioned wrinkle recovery angle-warp + fill directions (279 for treated vs. 247 for untreated); (d) residual static charge in ohms x 10⁸ at 65% relative humidity (1,800 for treated vs. 39,000 for untreated); (e) % moisture regain after 12 hrs. (24.8 for treated vs. 3.5 for untreated).

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EXAMPLE 28

Incorporation of Polyethylene Glycol
(av. mol. wt. 1,000) into Paper Products by its
Reaction with Crosslinking Agents

Commercial paper towels (reinforced with polyamide fibers in both directions) (2.1 oz/yd²) were treated with the PEG-1,000 with identical compositions as that described in Example 25 to a wet pickup of 137%, utilizing 30 lb. pressure to remove excess liquid from the paper. Subsequent drying for 7 min. at 70°C and curing for 2 min. at 150°C producing after washing in warm water and liquid detergent and air-drying to constant weight, a treated paper towel with a wt. gain of 39%.

The treated paper towel had a thermal storage value of 15.4 cal/g in the range of -3 to +37°C (on heating) and a thermal release value of 20.7 cal/g in the range of +22 to -18°C (on cooling). In contrast, the untreated paper towel had thermal storage and release values of 11.6 cal/g and 11.0 cal/g, respectively, in the same temperature ranges due only to the specific heat of the cellulosic and polyamide fibers in the towel. After 12 hrs. the moisture regain for the treated paper towel was 26.5% and only 8.5% for the untreated paper towel.

EXAMPLE 29

Incorporation of Polyethylene Glycol
(av. mol. wt. 8,000) into Cotton/Polyester
Fabric by Reaction with Crosslinking Agents

Two pieces of 50/50 cotton/polyester printcloth (4.1 oz/yd²) were immersed in (a) 45% aq. polyethylene glycol 8,000/10% DMDHEU/0.78% mixed catalyst (0.5% p-toluenesulfonic acid-0.25% MgCl₂-0.03% citric acid) and (b) 45% aq. PEG-8,000/10% DMDHEU at 30°C,

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1 put through squeeze rollers at 40 lb. pressure to a wet
2 pickup of 90%, then dried 5 min. at 85°C and cured 2 min.
3 at 140°C. After washing in hot water (60°C) and liquid
4 detergent and tumble drying, the first fabric had a
5 weight gain of 43% and the second fabric did not retain
6 the polyol and had no weight gain.

7 The thermal storage value of the first fabric (on
8 heating) in the temperature range of 32-77°C was 20.0
9 cal/g and its thermal release value (on cooling) in the
10 temperature range of 47 to 7°C was 18.5 cal/g, and
11 characterized by sharp endotherms on heating and sharp
12 exotherms on cooling. In contrast, the second fabric
13 (one not treated in the presence of an acid catalyst) in
14 the same temperature intervals exhibited thermal storage
15 values of 12.3 cal/g and thermal release values of 11.3
16 cal/g due only to the specific heat of the untreated
17 fabric.

18 EXAMPLE 30

19 Incorporation of Polyethylene Glycol 20 (av. mol. wt. 20,000) into Acrylic Fleece 21 Fabric by Reaction with Crosslinking Agents

22 Acrylic fleece fabric (5.2 oz/yd²) was immersed in
23 (a) 40% aq. polyethylene glycol 20,000/10% DMDHEU/0.76%
24 mixed catalyst (0.5% p-toluenesulfonic acid-0.25%
25 MgCl₂-0.01% citric acid), put through squeeze rollers at
26 40 lb. pressure to a wet pickup of 206%, then dried 5
27 min. at 85°C and cured 2 min. at 140°C. After washing in
28 hot water (60°C) and liquid detergent and drying in a
29 force draft oven to constant weight, the modified acrylic
30 fabric had a weight gain after conditioning of 89%.

31 Its thermal storage value (on heating) in the
32 temperature range of 32-77°C was 25.6 cal/g and its
33 thermal release value (on cooling) in the temperature
34 range of 57 to 17°C was 23.2 cal/g, and characterized

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1 by sharp endotherms on heating and sharp exotherms on
2 cooling. In contrast, untreated acrylic fabric in the
3 same temperature intervals exhibited thermal storage
4 values of 11.6 cal/g and thermal release values of 11.5
5 cal/g due only to the specific heat of the untreated
6 fabric. Percent reflectance values of the treated fabric
7 (as in Example 23) were 96% after soiling and one
8 laundering compared to only 65% for the untreated fabric
9 under comparable conditions.

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1 WE CLAIM:

2 1. A process for imparting improved properties
3 to non-hollow textile fibers comprising cross-linking
4 polyethylene glycol to said fibers, wherein the degree of
5 said cross-linking makes said polyethylene glycol water
6 insoluble, wherein said polyethylene glycol is present in
7 an amount sufficient to impregnate said fibers.

8 2. The process of Claim 1 wherein said
9 polyethylene glycol is impregnated on said fibers in an
10 amount of at least 0.25 grams per gram of fiber, wherein
11 said degree of cross-linking permits said polyethylene
12 glycol to change phases upon heating and cooling.

13 3. The process of Claim 1 wherein said fibers
14 are selected from the group consisting of cotton, rayon,
15 wool, polyamide, polyester, polypropylene, acrylic,
16 glass, and blends thereof.

17 4. The process of Claim 1 wherein polyethylene
18 glycol is applied to said fibers from an aqueous
19 solution, wherein said fibers thereafter are dried to
20 remove water, and wherein said fibers thereafter are
21 heated at a temperature sufficient to cross-link said
22 polyethylene glycol.

23 5. A process for imparting improved properties
24 to non-hollow textile fibers comprising cross-linking
25 polyethylene glycol to said fibers, wherein the degree of
26 said cross-linking makes said polyethylene glycol water
27 insoluble, wherein said polyethylene glycol is present in
28 an amount sufficient to impregnate said fibers with at
29 least 0.15 grams thereof per gram of fiber.

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1 6. The process of Claim 5 wherein said
2 polyethylene glycol is impregnated on said fibers in an
3 amount of at least 0.25 grams per gram of fiber, wherein
4 said degree of cross-linking permits said polyethylene
5 glycol to change phases upon heating and cooling.

6 7. The process of Claim 5 wherein said fibers are
7 selected from the group consisting of cotton, rayon,
8 wool, polyamide, polyester, polypropylene, acrylic,
9 glass, and blends thereof.

10 8. The process of Claim 6 wherein said fibers are
11 selected from the group consisting of cotton, rayon,
12 wool, polyamide, polyester, polypropylene, acrylic,
13 glass, and blends thereof.

14 9. The process of Claim 7 wherein polyethylene
15 glycol is applied to said fibers from an aqueous
16 solution, wherein said fibers thereafter are dried to
17 remove water, and wherein said fibers thereafter are
18 heated at a temperature of about 100-170 C to cross-link
19 said polyethylene glycol.

20 10. The process of Claim 8 wherein polyethylene
21 glycol is applied to said fibers from an aqueous
22 solution, wherein said fibers thereafter are dried to
23 remove water, and wherein said fibers thereafter are
24 heated at a temperature of about 100-170 C to cross-link
25 said polyethylene glycol.

26 11. The process of Claim 9 wherein said
27 temperature is about 100-130 C.

28 12. The process of Claim 10 wherein said
29 temperature is about 100-130 C.

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1 13. The process of Claim 9 wherein said
2 polyethylene glycol has a molecular weight of greater
3 than 1500, and wherein p-toluenesulfonic acid is included
4 in said solution as an acid catalyst.

5 14. The process of Claim 10 wherein said
6 polyethylene glycol has a molecular weight of greater
7 than 1500, and wherein p-toluenesulfonic acid is included
8 in said solution as an acid catalyst.

9 15. The process of Claim 10 wherein said
10 polyethylene glycol-impregnated fibers have improved
11 properties as to soil release, durable press, resistance
12 to static charge, abrasion resistance, pilling resistance
13 and water absorbency.

14 16. A process for imparting improved properties to
15 non-hollow cellulosic fibers comprising cross-linking
16 polyethylene glycol to said fibers, wherein the degree of
17 cross-linking makes said polyethylene glycol water
18 insoluble, wherein said polyethylene glycol is present in
19 an amount sufficient to impregnate said fibers with at
20 least 0.15 grams thereof per gram of fiber.

21 17. The process of Claim 16 wherein said
22 polyethylene glycol is present in amount of at least 0.25
23 grams per gram of fiber, and wherein said degree of
24 cross-linking permits said polyethylene glycol to change
25 phases upon heating and cooling.

26 18. The process of Claim 16 wherein said
27 polyethylene glycol is applied to said fibers from an

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1 aqueous solution, wherein said fibers thereafter are
2 dried to remove water, wherein said fibers thereafter are
3 heated to about 100-170 C to cross-link said polyethylene
4 glycol.

5 19. The process of Claim 17 wherein said
6 polyethylene glycol is applied to said fibers from an
7 aqueous solution, wherein said fibers thereafter are
8 dried to remove water, wherein said fibers thereafter are
9 heated to about 100-170 C to cross-link said polyethylene
10 glycol.

11 20. The process of Claim 18 wherein said
12 temperature is about 100-130 C.

13 21. The process of Claim 19 wherein said
14 temperature is about 100-130 C.

15 22. The process of Claim 20 wherein said fiber is
16 paper or wood pulp fiber.

17 23. The process of Claim 21 wherein said fiber is
18 paper or wood pulp fiber.

19 24. The process of Claim 18 wherein said
20 polyethylene glycol has a molecular weight of greater
21 than 1500, and wherein p-toluenesulfonic acid is included
22 in said solution as an acid catalyst.

23 25. The process of Claim 19 wherein said
24 polyethylene glycol has a molecular weight of greater
25 than 1500, and wherein p-toluenesulfonic acid is included
26 in said solution as an acid catalyst.

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1 26. The process of Claim 20 wherein said
2 impregnated fibers have improved properties as to soil
3 release, durable press, resistance to static charge,
4 abrasion resistance, pilling resistance and water
5 absorbency.

6 27. Non-hollow textile fibers impregnated with
7 cross-linked polyethylene glycol wherein the degrees of
8 cross-linking makes said polyethylene glycol water
9 insoluble.

10 28. The invention of Claim 27 wherein said
11 polyethylene glycol is present in an amount of at least
12 0.25 grams per gram of fiber, and where the degree of
13 cross-linking is sufficient to permit said polyethylene
14 glycol to change phases upon heating and cooling.

15 29. The invention of Claim 27 wherein said fibers
16 are selected from the group consisting of cotton, rayon,
17 wool, polyamide, polyester, polypropylene, acrylic,
18 glass, and blends thereof.

19 30. Non-hollow textile fibers impregnated with at
20 least 0.15 grams of cross-linked polyethylene glycol per
21 gram of fiber, wherein the degree of cross-linking makes
22 said polyethylene glycol water insoluble.

23 31. The invention of Claim 30 wherein said
24 polyethylene glycol is present in an amount of at least
25 0.25 grams per gram of fiber, and where the degree of
26 cross-linking is sufficient to permit said polyethylene
27 glycol to change phases upon heating and cooling.

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1 32. The invention of Claim 30 wherein said fibers
2 are selected from the group consisting of cotton, rayon,
3 wool, polyamide, polyester, polypropylene, acrylic,
4 glass, and blends thereof.

5 33. The invention of Claim 31 wherein said fibers
6 are selected from the group consisting of cotton, rayon,
7 wool, polyamide, polyester, polypropylene, acrylic,
8 glass, and blends thereof.

9 34. The invention of Claim 30 wherein said
10 impregnated fibers have improved properties as to soil
11 release, durable press, resistance to static charge,
12 abrasion resistance, pilling resistance and water
13 absorbency.

14 35. The invention of Claim 31 wherein said
15 impregnated fibers have improved properties as to soil
16 release, durable press, resistance to static charge,
17 abrasion resistance, pilling resistance and water
18 absorbency.

19 36. The invention of Claim 30 wherein said
20 polyethylene glycol has a molecular weight of greater
21 than 1500.

22 37. The invention of Claim 31 wherein said
23 polyethylene glycol has a molecular weight of greater
24 than 1500.

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1 38. The invention of Claim 35 wherein said fibers
2 are selected from the group consisting of cotton, rayon,
3 wool, polyamide, polyester, polypropylene, acrylic,
4 glass, and blends thereof.

5 39. Non-hollow cellulosic fibers impregnated with
6 at least 0.15 grams of cross-linked polyethylene glycol
7 per gram of fiber, wherein the degree of cross-linking
8 makes the polyethylene glycol water insoluble.

9 40. The invention of Claim 39 wherein said
10 polyethylene glycol is present in an amount of at least
11 0.25 grams per gram of fiber, and wherein the degree of
12 cross-linking permits the polyethylene glycol to change
13 phases upon heating and cooling.

14 41. The invention of Claim 39 wherein said fibers
15 are paper or wood pulp fibers.

16 42. The invention of Claim 40 wherein said fibers
17 are paper or wood pulp fibers.

18 43. The invention of Claim 39 wherein said
19 impregnated fibers have improved properties as to soil
20 release, durable press, resistance to static charge,
21 abrasion resistance, pilling resistance and water
22 absorbency.

23 44. The invention of Claim 40 wherein said
24 impregnated fibers have improved properties as to soil
25 release, durable press, resistance to static charge,
26 abrasion resistance, pilling resistance and water
27 absorbency.

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1 45. The invention of Claim 39 wherein the
2 molecular weight of said polyethylene glycol is greater
3 than 1500.

4 46. The invention of Claim 40 wherein the
5 molecular weight of said polyethylene glycol is greater
6 than 1500.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US87/01472

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. BC5D 3/02; DC2G 3/00		
U.S. CL. 427/394, 400; 428/375, 396, 913		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	427/394, 400; 428/375, 396, 913	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category [*]	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US, A, 3,607,591 (HANSEN) 21 SEPTEMBER 1971	1-46
A	US, A, 4,572,864 (BENSEN) 25 FEBRUARY 1986	1-46
A	US, A, 4,587,279 (SALYER) 06 MAY 1986	1-46
<p>[*] Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹		Date of Mailing of this International Search Report ²
22 SEPTEMBER 1987		01 OCT 1987
International Searching Authority ¹		Signature of Authorized Officer ¹⁰
ISA/US		W.J. VanBalen

